DESIGN OF A MOLECULAR MEMORY DEVICE:
THE ELECTRON TRANSFER SHIFT REGISTER MEMORY

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ABSTRACT

A molecular shift register memory at the molecular level is described. The memory elements consist of molecules can exit in either an oxidized or reduced ("1" or "0") state and the bits (electrons) are shifted between the cells with photoinduced electron transfer reactions. The device integrates designed molecules onto a very large scale integrated (silicon microelectronic) substrate, providing an example of an ultrasmall electronic device which could actually be made. Strategies for implementing the device are discussed,

INTRODUCTION

It is clear from these proceedings that the field of molecular electronics has moved away from target devices which fully exploit molecular sizes [1-6] to novel devices based on ensembles of molecules with novel switching properties (photochromism, channel controlling, etc.). This shift in emphasis was caused by the difficulty of implementing proposed molecular systems and the fact that ensembles of relatively simple chemical and biochemical systems can be reversibly switched between states, and these properties exploited, However, the prospects of designing devices from molecules up and of truly exploiting molecular sizes remains very appealing

The absence of suggestions for structures which are synthetically approachable and functions which are in the realm of existing well understood physical chemistry has made the possibility of implementing a molecular device quite unlikely [7]. In this paper we present the design of a molecular size shift register memory element based on electron transfer reactions. The molecular elements could actually be fabricated using known strategies of organic synthesis and interfaced with conventional microelectronic technology [8], Such work could provide real progress towards achieving devices with energy costs (per bit pro-

cessed) approaching the energies of single molecule electronic or confirmational energy transitions (a few eV or less) [1,9] and information storage densities much larger than available with existing technologies. Most importantly, this memory element may be an example of a molecular size electronic device which could actually be made.

DESIGN OF A MOLECULAR ELECTRONIC DEVICE

The essential questions which must be addressed when designing a molecular electronic device which will function are: How is the energy to be supplied at a molecular level? How does the clock signal get to the molecular device? How are the molecular devices to be interconnected, and how are the connections to be chemically fabricated? How is communi cation between the molecular size features of a chip and the molecular device to be achieved? How are errors to be dealt with? The molecular shift register described below answers all of these design questions,

THE ELECTRON TRANSFER MOLECULAR SHIFT REGISTER

Shift register memories consist of memory cells connected in a line. During each clock cycle, information is written at the left terminal cell and the contents of each cell are shifted one unit down the chain to the right. One bit of information is also read out at the right terminal cell.

electrons in — | D_1 | A_1 |—| D_2 | A_2 |—| D3 | A3 | ∘∘∘ electrons Ont
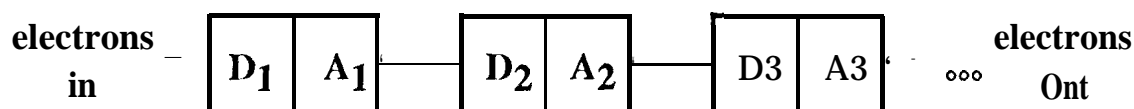
Figure 1. A schematic representation of the the cells in a shift
register memory are shown, Here the information would
be written with electrons.

Shift registers are used in conventional memory elements (magnetic bubble memories are shift registers) and information delay lines. Here, we will describe implementations where the infromation in a given cell is written by the presence ("l") or absence ("O") of an electron,

One of the simplest molecular switching process is electron transfer. Electron transfer involves moving a relatively well localized electron from the donor (D) to the acceptor (A) without breaking or forming any chemical bonds. Because the rates of electron transfer reactions are sensitive functions of reaction free energy, vibronic coupling, and distance [10], the rates of these reactions can be tuned over many orders of magnitude, The transfer may be either permanent or reversible.

A shift register could be built from a one-dimensional array of DA molecules as shown in Figure 2. D has an accessible excited state from which the electron transfer to A occurs followed by the shifting of the electron to the next cell to the right. Information is written on the left side of the chain (one bit at a time) and advances down the chain one unit per clock cycle (light flash).
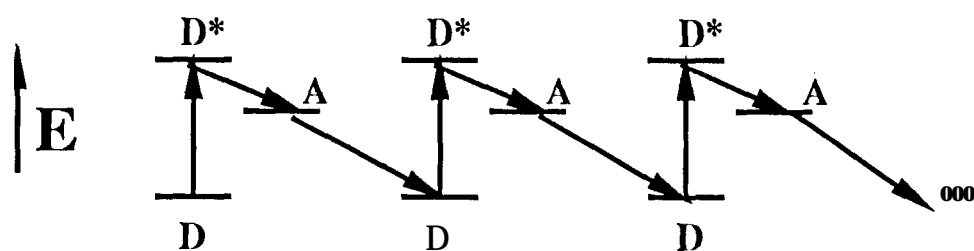

Figure 2. The donor and acceptor levels in a typical shift register polymer are shown. The donors have accessible ground and excitied states. Intermediate states are suppressed in this representation.

This scheme solves the design requirements in the following way: the energy is provided by light; the clock signal is provided by pulsing the light; the chemistry for linking donors and acceptors is known; interconnections with silicon may be provided by appropriate surface binding groups; errors can be dealt with to some degree with multiple chains or methods described below. Information in this implementation is written and read at electrodes bound to the first and last groups of the polymer.

The internal details of each unit will be more complicated than suggested by Figure 2, but it shows the three characteristic time-scales of the system, These are the time for charge separation within a single cell containing DA (τ_c), the lifetime of the charge separated state in an isolated DA unit (τ_r), and the time for the charge to be shifted to the adjacent cell to the right (τ_s).

Existing donor-acceptor model compounds suggest that typical monomer units with appropriate rates would be roughly 20 Å long. Interfacing with micron scale architecture, then, would require DA chains of about 600 repeat units (bits) or longer, Chains comprised of these units would be bound between two electrodes on a VLSI substrate [11] and immersed in a solution to maintain a Debye length of roughly 20 Å. To simplify detection of the arriving electrons, roughly 5000 identical chains would be needed between the electrodes [11]. Smaller numbers could be used but then the signal would require external amplification, The 5000 chain redundancy also provides a means of error correction. The redundancy allows averaging of the signal at the receiving electrode over all of the chains.

For half of the written electrons to arrive at the receiving electrode after 600 hops, the efficiency of transfer at each of the 600 steps must be greater than or equal to 99.9%. Biological photosynthetic systems suggest that such efficiency may be achievable in tailored systems [12], Strategies which give each electron several chances to transfer are possible, in

addition to simply optimizing the rate of forward reactions relative to recombination reactions. Other strategies to keep the electrons moving along parallel chains in synchrony (analogous to cooperativity in biological systems), or to provide some form of "molecular" charge amplification, are also under study. The 99.9% efficiency requirement can probably be satisfied in real systems by manipulating the duration of the excitation pulse. Pulses must be shorter than τ_s in duration to avoid multiple electron transfer steps down the chain during a flash, Pulses of length $\tau < \tau_s$ would provide $\sim \tau/\tau_c$ "chances" for the electron to transfer. Thus, if the donor is excited three times, and it has a 90% chance of electron transfer per excitation, the 99.9% efficiency constraint is satisfied. Polymers with more complicated repeat units and multiple wavelength excitation schemes might also be used to increase the efficiency [8].

MOLECULAR IMPLEMENTATIONS SCHEMES

Two orbital energy level schemes are now given which would provide proper shifting of information. In the first scheme, Figure 3a, bits are written as electrons which move from left to right in the register. Three electron localization sites per cell, rather than two, provide greater adjustability in the charge separation and recombination rates as well as enhanced efficiency. In the second example, Figure 3b, the bits are written as "holes" which move from left to right. By inverting the energy level diagrams and replacing electrons with "holes" analogous implementations are also possible [8].
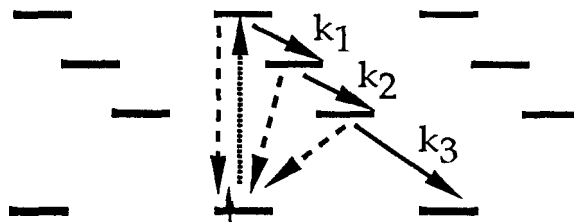

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Figure 3a. In this scheme a donor, primary acceptor, and secondary acceptor are used in each cell. Donor excitation initiates the electron transport. The string "O1O" is written. The "l" (presence of an electron) on the central cell is indicated by a small vertical arrow.

Possible molecular implementations [8a] of the schemes in Figures 3a and 3b using electron donors and acceptors known from the photosynthetic model compound (Figure 4) or solar energy conversion literature [13] were discussed. These are meant as illustrations of the kinds of systems which might be of use. Modifications may be needed to produce cells with the proper balance of forward and reverse rates, Such modifications are most easily provided for given donors and acceptors by changing the length or degree of saturation of the bridge connecting them or by changing the free energy of the transfer reactions by attaching electron donating or withdrawing groups to the donors and/or acceptors. Rates can be tuned over many orders of magnitude by a combination of these effects for a given donor-acceptor pair.
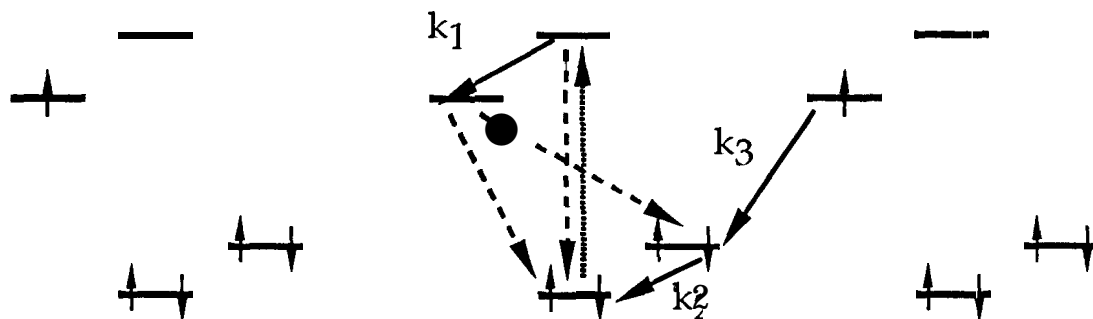

Figure 3b. In this scheme a donor, intermediate, and acceptor are used in each repeat unit. Intermediate excitation initiates the electron transport. The string "O1O" is written, The information is stored on the unit on the far left in each cell and a "l" is written as a hole at this site. The holes move from left two right during a clock cycle.

Other strategies for building up the shift register structures might include attaching chromophores to DNA [14], or building up Langmuir

Blodgett films of the chromophores [15]. Also, relatively rigid organic polymers to which the chromophores could reattached might also beef use [16].
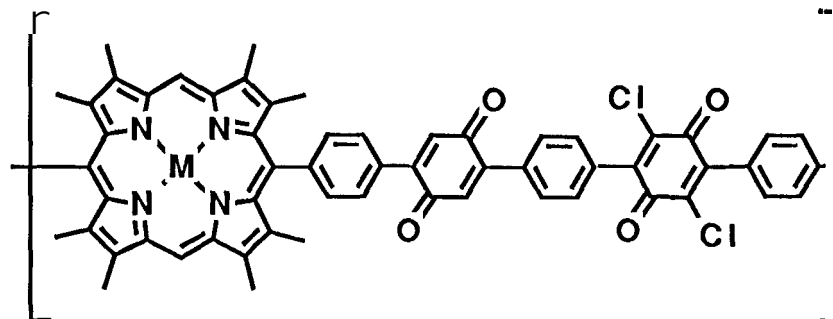

Figure4. A possible molecular implementations of the scheme in Figure 3a for the shift register polymer is shown. Ref. 8a gives an implementation of the energy level scheme in Figure 3b. The crucial transfer rates can be modified by introducing substituents onto the porphyrin and quinones or by modifying the bridging groups, A small molecule similar to this reported in 13c.

PERSPECTIVES

One might have expected that moving from the micrometer to the nanometer size scale would cause uncertainty limitations on switching events and the loss of information purity in real systems. (On this size scale events need not be purely deterministic because of quantum effects), Also, there is the problem of coupling molecular size devices to macroscopic electronic components. For these reasons, one might have expected the need to work with ensembles of molecules and to move away from the truly molecular regime. However, if we can guarantee very high probabilities for the desired directionality of the reactions, as discussed above, there is no need for an ensemble of molecules to avoid the uncertainty limitations, The constraint of extremely high transfer probabilities may restrict the permissible values of τ_c, τ_r, and τ_s, and therefore the kinds of allowable structures, but the systems should be buildable.

The issues of charge amplification and error correction must be answered if one wants to decrease the size of the device further (beyond several thousand identical chains) and decrease its energy consumption (to "molecular" energies of -50 kT per bit processed). This can be achieved by including a mechanism to correct error propagation every few units in the chain, and by introducing some kind of molecular size charge amplifier to couple the microscopic device to macroscopic c components.

In this initial description of a molecular shift register with 600 monomer groups, we need 99,9% efficiency for electron transfer between cells to guarantee that half of the electrons arrive at the receiving electrode at the proper time, Therefore, the errors propagate over the full length of the chains and "error correction" is only performed at the reading electrode. Including units to restore electrons to their proper places in the polymer would substantially improve the device performance. One way that this can be implemented is by building the system of roughly 10 polymer chains, and at a restoration step putting all corresponding cells of the system into the majority state of the cells. Such an implementation would also permit building an operational device with transfer efficiencies less than 99.9%,

The restoration described above may allow a device free of error limitations to be composed of a small number of chains. However, this does not solve the requirement of several thousand electrons at the receiving electrode so that the signal can be easily read. Eventually, the way to solve this problem is not by carrying 5000 electrons along the full length of the chains. Rather, the number of chains should be kept small and, near the chain ends, the charge should be amplified prior to arrival at the receiving electrode. One strategy to achieve this amplification is through a molecular fork structure [8]. A molecular fork is conceived as a unit in the chain at which the arrival of a single electron results in the departure of two electrons and a hole moving away on separate branches.

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An assembly of such units would amplify one electron into 1000 in 10 branching. Fewer than 10 polymer strands, each with such a branched treelike structure at the end, would provide the needed number of electrons. Other charge amplification schemes are conceivable. For example, the arrival of a few electrons might induce a channel in a membrane to open releasing a large number of signaling species.

These two schemes, information restoration and charge amplification, can only be implementedif we have a reservoir of charge available. In some biological processes, such as photosynthesis and respiration, charge equilibration is performed by sophisticated mechanisms [12]. When designing our fork, the simplest mechanism will probably involve electron transfer with species in solution, One way to couple the reservoir of charge to the device is by having some units of the fork structure with energy levels capable of giving (or receiving) electrons to the solution. Light can be used to inject (or remove) the electrons from these inter-mediate units to the rest of the fork at the appropriate times, A strategy for making these intermediate units more effective is to guarantee that they can exchange only two or more electrons with the solution, By doing this, no group in the solution will be able to donate electrons to the shift register cells themselves, so the further introduction of errors will be avoided, This may be achieved by using molecules that have stable redox states differing by two electrons, or by some cooperative mechanism of electron transfer. With this strategy there is no way that exchange of electrons between the device and the solution will effect the processing of information, which is a one-electron (or hole) transition.

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